Report 6. Interrogation of Prof. Dr. F. Martin.

Introduction.

Prof. Martin was President of the Vorstand (Directorate) of the Ruhrchemie A.G., the other members being Dr. Hagemann (chemist) Herr von Asboth (engineer) and Herr Waibel (financier).

Martin, therefore, headed the list of key men relating to the Target under investigation and his interrogation was of particular importance. He was located at a farm near Gebhartshagen in the Braunschweig area by 30 A.U., R.N. and, together with Dr. Hagemann, was brought by them to Brussels en route for London.

In Brussels, members of the C.I.O.S. Item 30 Ruhr team were able to interview Martin before his departure for London. The report of this interview is given below followed by a record of additional information obtained as a result of subsequent interviews held in London.

Interview in Brussels on April 22nd, 1945.

Personnel conducting Interrogation:

Lt. Col. A. Parker, British, Ministry of Fuel and Power
Dr. A.R. Powell, U.S., Petroleum Administration for War
Capt. C.C. Hall, British, Ministry of Fuel and Power.

Reported by: Dr. A.R. Powell, U.S., Petroleum Administration for War.

General Assessment of Fischer-Tropsch Process:

Martin stated that he believed the Fischer-Tropsch process would be of no present value for production only of motor fuel in a free world economy. Under such conditions, he believes the process is of value only for manufacture of special chemicals or upgraded products commanding a considerably higher unit sales value than does motor fuel. He stated that some of these special applications of the Fischer-Tropsch process had been described by a Dr. Asinger in Zeitschrift für (angewandte) Chemie about five months prior. Some of these special applications were mentioned by Martin later in the interview.

Synthesis Gas:

Martin said that he favored the production of the synthesis gas for Fischer-Tropsch plants by the original process of using coke as fuel in water-gas generators, followed by partial conversion of the carbon monoxide to obtain the correct hydrogen-carbon monoxide ratio. This method of synthesis gas manufacture had always been used at the Sterkrade plant of Ruhrchemie, and for the most part had been used in the other Fischer-Tropsch plants located in the Ruhr area. At the time these plants were started, coke manufacturers in the Ruhr were seeking sales outlets for coke other than the usual consumption in blast furnaces and this situation largely determined the fuel policy at that time. However, Martin said that he still preferred coke as the raw material instead of the somewhat cheaper raw coal or brown coal since coke was clean, free of tarry matter, could be gasified with relatively simple and trouble-proof equipment, and allowed easier and more accurate control of the composition of the synthesis gas.

Martin stated that the various processes for making synthesis gas from brown coal or by the cracking or reforming of coke-oven gas always gave operating troubles due to the presence or deposition of tar, carbon, resins and other disturbing substances. The presence of resin-formers in such gas led to the fouling of the catalyst for removal of organic sulphur, and the necessity in such cases of installing active carbon chambers before the organic-sulphur-removal equipment to free the gas of these harmful compounds.

Despite his preference for the coke water gas method of making synthesis gas, Martin believed much could be done to improve the process. Specifically, he thought water gas generators, using coke as fuel, should get away from the usual cyclic manner of operation and should operate continuously, for example by using oxygen and steam. This would avoid some difficulties encountered at the Sterkrade plant, such as mechanical troubles, dilution of the gas with nitrogen etc. He admitted that this was an unsolved problem at present.

Martin was asked about the present status of the Wintershall-Schmalfeldt process for making synthesis gas from finely pulverized coal. He stated that the process was in experimental full-scale operation, but that the process now uses some oxygen in its operation, which was not true of the original Wintershall-Schmalfeldt process as described in the literature.

Martin also briefly commented on the production of synthesis gas from coke oven gas, which had been experimented with by Bamag. He mentioned that they used steam rather than carbon dioxide as the reaction between methane and carbon dioxide was too slow.

Martin was asked about the possibilities of using coke-oven gas directly as a synthesis gas in the catalyst chambers. He said that this had been tried but one of the chief difficulties had been the complete removal of the organic sulphur from the gas since coke-oven gas contains thiophenes which are difficult to remove and also even the carbon bisulphide and carbon oxysulphide had been difficult to destroy, due to the bad effect of coke-oven gas hydrocarbons on the organic sulphur catalyst. For a reasonable life of the Fischer-Tropsch catalyst, it would be necessary to remove all sulphur and cyanogen compounds from the gas. In this connection he mentioned that Ruhrgas had erected a plant near Essen (based on Ruhrchemie research work) to catalytically treat coke-oven gas over a nickel catalyst so as to increase the methane content by interaction of hydrogen and carbon monoxide. By this scheme, they increased the heating value of the gas from 4,000 K cal/m^3 to 6,000 K cal/m^3. The object was the production of "Treibgaz" for motor transport.

Catalysts:

Martin stated that the cobalt catalyst is still the favorite for most purposes, and had not been displaced by the iron catalyst by any means. Cobalt catalysts were easy to make and were reliable in operation. The iron catalyst had been proposed largely as a war-time substitute for cobalt which was in short supply in Germany, due to the war. If the Ruhrchemie were to project a Fischer-Tropsch plant today, with free access to world market metals, they would recommend the cobalt catalyst.

Martin stated that they had discovered that the life of the cobalt catalyst could be materially lengthened by strict attention to thoroughness of purification of gas from sulphur, and that this life would now average 5 to 6 months. Regarding regeneration of the cobalt catalyst, Martin said there was a loss of four per cent per regeneration, but he felt confident this could be decreased to two per cent.

Asked about the most important factor involved in the manufacture of catalyst, Martin stated that the reduction step was the most critical and that the washing step was second in importance.

Martin was then asked about the known policy of Ruhrchemie in substituting magnesia for a part of the thoria in the cobalt catalyst. He stated that the full amount of thoria in the catalyst produced more paraffin and that any substitution of thoria by magnesia decreased this production. The magnesia was added solely to improve the physical characteristics of the catalyst. It had the effect of making the catalyst particle harder and less subject to disintegration to a dust. It was necessary to reach a compromise between the relative proportion of thoria and magnesia in order to obtain both a reasonably high production and good physical quality in the catalyst.

Martin stated that Dr. Gehrke, formerly in charge of catalyst manufacture at Sterkrade, had left and that he did not know his present location.

Martin stated that they had about 100 small, catalyst testing units in the laboratories at Sterkrade. These were constructed on the 'aluminium-block' principle and had a catalyst capacity of 50-100 ml. Each large-scale batch of catalyst was tested in these units using a standard temperature* and fixed gas rate (1 litre /g.Co /hour) at atmospheric pressure. If the yield of products remained approximately constant for about 14 days under the conditions of this test, then they could confidently predict from their experience that the batch under test would give a satisfactory performance in the full-scale ovens.

However, the test could be applied only to catalysts of similar composition and would not be applicable to any radically different catalyst on which there was no plant data.

In another phase of the interrogation, Martin

* Martin gave this temperature as 'about 190°C.,' but documents found in the laboratories at Sterkrade indicated a figure of 185°C., which is much more probable.

was asked about iron catalysts. Martin reviewed the statement of Dr. Franz Fischer that a temperature of 240° was necessary for successful operation with the iron catalyst. Such a temperature required a water pressure in the cooling system of the catalyst chamber of 30 atmospheres. Since such a pressure presented many construction problems, it was most desirable to obtain an iron catalyst that would operate at a lower temperature. By a special process developed by Ruhr-chemie, an iron catalyst was produced that could operate at 215-225° (average 220°) and the pressure then was such that the concentric double tube catalyst chambers of the medium-pressure process could be used.

This catalyst contained for every 100 parts of iron, 30 parts of kieselguhr, about 3-4 parts of copper (Cu) and 10 parts lime (CaO). Increase in the proportion of copper gives harder catalysts which yield more wax but also more alcohols. For the preparation, the metals are dissolved in nitric acid and precipitated rapidly from hot solutions using potassium carbonate. Martin stressed the necessity for using potassium and not sodium as the alkali. After precipitation the precipitate is washed until samples taken from the filter show a pH of 8.0. If this point is over-shot, the pH is brought back by the addition of a weak potassium carbonate solution.

The amount of nitric acid involved in the preparation and the necessity for using potassium for the precipitation, makes the iron catalyst more expensive to prepare than cobalt. The difference in cost can be somewhat reduced by recovering potassium nitrate from the filtrate and wash waters.

The reduction of this material is less critical than that of the cobalt catalyst and is carried out at 325-350° for a somewhat longer time than the cobalt reduction. As in the case of cobalt, the iron catalyst must be only partially reduced, about 60 to 70%, since the presence of some iron oxide seems to be essential to the efficient working of the catalyst.

Martin believes that the use of potassium carbonate causes a metamorphism of the iron oxides and hydroxides into a form that makes the catalyst more effective at lower temperature. Ruhrchemie had operated a pilot plant with the iron catalyst, using 100 m^3/hr. synthesis gas for about a year. Experience with this pilot plant had furnished the data for the Italian project which had been set up for use of iron catalyst.

Martin stated at this juncture that results obtained on the 100m^3 /hr. scale were closely comparable with the full scale, but added that this was the minimum scale which gave fully reliable prediction of full-scale performance.

Martin was asked about the sintered iron catalyst of I.G. He said that I.G. had used this sintered iron catalyst exclusively for the manufacture of C_9 alcohols for plasticizers etc. and that this had no relation to the Fischer-Tropsch process as ordinarily conducted. As an aside at this point, Martin said that the Fischer-Tropsch process had been offered to I.G. in 1930 for about 500,000 marks, but that they had refused it.

Operation of Catalyst Chambers:

Martin was interrogated on capacity of catalyst chambers and yield of primary products and the relationship between yield and rate of gas throughput. He said that each chamber contains one metric ton of cobalt and produces 1.5 metric ton of primary product per day on the average, including chambers in all stages. The main objective is to utilize the synthesis gas at the highest efficiency consistent with reasonable capacity per chamber since synthesis gas is expensive. The normal operating rate will produce a yield of 150 g. primary product per m^3 of ideal synthesis gas. Some plants use a lower operating rate and thereby attain yields as high as 165 g. per m^3. In each case, a proper balance must be maintained between fuel cost and capital charges on equipment. For the 150 g. per m^3 yield noted above, synthesis gas flow is 1000 m^3 per metric ton of cobalt per hour in the first stage chambers, but as the catalyst becomes older, this rate is lowered until it is 800 m^3 per ton per hour just before regeneration of the catalyst. When operating to the higher yield, the initial rate is 900 m^3 and the final rate 700 m^3 per hour. The general policy of chamber rotation is to put fresh catalyst in the last stage in contact with older gas while older catalyst is put into the first stage in contact with fresh synthesis gas.

Martin was then asked whether normal-pressure or medium-pressure operation was best. He explained that each plant had been given a free choice as to which system it desired. The medium-pressure system has the advantage of giving three times as much hard paraffin as does the normal-pressure, and hard paraffin can be used for the manufacture of higher alcohols, such as C_{25}, which form valuable neutral emulsifying agents and can be made by no other process. Also the medium-pressure operation gives a somewhat longer catalyst life (about 2 months). The normal-pressure process gives a high yield of benzin (gasoline or petrol), but under peace conditions and a free world economy such benzin could not compete with that made from natural petroleum, so this is no advantage. Summing up, Martin said that the medium-pressure process should be chosen for any post-war project.

Martin was then asked about the use of recirculation with the cobalt catalyst and he gave information fully corroborating that previously obtained from Herr Alberts.

On the method of operating with the iron catalyst, Martin said that water gas was used as the raw material with a recirculation of two parts residual gas to one part fresh gas. The gas rate was the same as that used for cobalt on an oven basis, i.e., 1000m^3 /oven /hr. of fresh gas. The average working temperature was 220°C.. The use of recirculation entirely suppressed the deposition of carbon on the catalyst which otherwise tended to occur when water-gas was used as raw material. Both water and carbon dioxide are oxygen products of the reaction.

For one stage with recirculation, the yield of products is about 110 g./m^3, and for two stages, about 150 g./m^3.

The steam drums in the Ruhrchemie catalyst chamber system limit the top temperature of operation to 225°C., and with this limiting temperature the life of the iron catalyst is 5-6 months. If a new plant was constructed without this limitation, a higher final temperature could be reached and a longer life be obtained.

The Ruhrchemie iron catalyst gives a high yield of wax, i.e., 40-50% of the primary product.

Iron catalysts suffer from the disadvantage of producing carbon dioxide which must be scrubbed out of the gas between the stages if excessive dilution of the stage 2 inlet gas is to be avoided, whereas with cobalt, the water, which is practically the sole oxygen product, can be removed simply by condensation.

Diesel Oil

Despite the excellent quality of the diesel oil recovered from Fischer-Tropsch primary products, Martin considered this a low-grade use of the product, emphasizing again Martin's opinion that Fischer-Tropsch primary products should be converted into more valuable materials, such as special chemicals. For example, he mentioned that I.G. had purchased the diesel oil fraction (B.P. 230°-320°) for the purpose of manufacturing detergents. The fact that this had been done in war time, when diesel oil was in critical demand, illustrated his point.

Questioned as to the possible increase in yield of the diesel oil fraction by some modification of the normal Fischer-Tropsch process, Martin said every effort to accomplish this had failed. In general, the maximum yield of this fraction by any type of operation was about 35 per cent.

High-Melting-Point Wax:

Martin was asked about the possible commercial production of high-melting-point wax by a ruthenium catalyst as proposed by Pichler. He said that he did not consider this commercially feasible because of the extreme scarcity of ruthenium. Martin said that such waxes could be produced more economically by means of the usual cobalt catalyst, although, of course, not in the 100% yield as had been claimed by Pichler for the ruthenium catalyst. Martin repeated the known claim that waxes with melting points as high as 90° or 95° could be recovered in a relatively small percentage from the primary products of the usual cobalt catalyst.

Martin stated that a method for increasing the yield of hard wax by means of the usual cobalt catalyst was to pass synthesis gas through the catalyst chambers at a considerably lower rate of flow and at a lower temperature. Following this, the hard wax could be extracted from the catalyst by means of benzin. Martin stated that the commercial demand for this special hard wax had been extremely small and was only of the order of one metric ton per month, so that it would not be a very important product unless new uses were discovered.

Synthetic Lubricating Oil:

Martin said that the quality of the lubricating oil made from Fischer-Tropsch primary products had been much improved since the beginning of the war. The oxidation test had been improved by the addition of inhibitors, the best one being phenathiazine (0.1 - 0.2%), or by treating the oil with elemental sulphur and aluminium chloride.

The best stock for lubricating oil was cracked material made from those fractions of the primary product boiling between 220° and 320° and wax with a melting point up to 30°. All material intended for this cracking step was filtered to remove the small amount of cobalt that had entered the oil from the catalyst, since it had been found that even the small amounts of cobalt caused undesirable side reactions during cracking. The cracking was carried out in a Dubbs unit in the presence of steam at a temperature under 500°C. This unit would operate for periods of 90 days before it was necessary to remove carbon. Martin said that all details of their synthetic lubricating oil process would be found in their documents, such as projects and correspondence, dealing with proposed Japanese plants.

The production of synthetic lubricating oil at the Sterkrade-Holten plant of Ruhrchemie had averaged 1400 metric tons per month. The yield of lubricating oil from the cracked product was about 55%, with about 25% going to gas. Most of the lubricating oil made had a viscosity of 6 to 7 degrees Engler and a viscosity pole height of 1.7, although attempts had been made to make higher viscosity oils by operating at lower temperature.

Martin stated that oil obtained by use of the iron catalyst had been considered good stock for production of lubricating oil without any preliminary cracking as was required for the product from normal Fischer-Tropsch operation. However, before the iron catalyst oil can be so used, it is necessary to remove all oxygen compounds. In the first laboratory tests, metallic sodium was used for this purpose. Later a catalytic process was developed that was considered to be more commercially feasible than use of sodium. The

Research on Direct Production of Higher Alcohols by Fischer-Tropsch Synthesis:

Martin said that small scale experiments conducted at a pressure of 200 atmospheres and a temperature of 200° showed a production of higher alcohols with excellent yields.

Martin was somewhat indefinite on the catalyst used but he believed that both cobalt, possibly containing a little zinc oxide, and an iron catalyst had been used in these experiments. The ratio of hydrogen to carbon monoxide in the synthesis gas used was 1.8 The product resulting contained as much as 80% alcohols, with the remaining 20% largely hydrocarbons and a small amount of fatty acids. The alcohols obtained were mainly in the range from C_7 to C_{12}, with smaller quantities of lower alcohols such as propanol and butanol and of higher alcohols above C_{12}. For the most part the alcohols were primary. By changing temperature, pressure, catalyst, etc., Martin is convinced that other proportions and types of alcohols could be made.

In this connection Martin mentioned that alcohols (mostly lower alcohols) were produced to some extent in the normal synthesis of hydrocarbons, and had been recovered from the reaction water. This had had much to do with initiating the above research.

Research on Direct Production of Fatty Acids by Fischer-Tropsch Synthesis:

The medium-pressure synthesis yields about 1% of directly synthesised fatty acids. About half of these are present in the diesel oil fraction and at Sterkrade-Holten about 3 tons per month of C_{11}- C_{18} acids had been recovered from the heavy diesel oil. Martin claimed that soap made from these acids was superior to that made by the Witten oxidation process in being free from objectionable odour. This claim, however, was certainly not substantiated by examination of a small sample of this soap which Martin had with him!

The value of these recovered acids had led to attempts to increase the yield, and some success had been achieved by the addition of small quantities of acetic acid to the synthesis gas. A 10% yield of acids had been obtained in this way.

catalyst was clay that had been treated with sulphuric acid and then heated. By passing the vapor of the lubricating oil stock over this catalyst at a temperature which never exceeded 350°, the oxygen compounds were destroyed without any undesirable shifting of double bonds that might have affected the usefulness of this oil for lubricating oil manufacture.

A man by the name of Clar had been in charge of lubricating oil manufacture at Sterkrade, but Martin did not know his present location. (See Report 9, p.94).

OXO Process:

Martin was not interrogated on technical details of the OXO process. He was, however, interrogated regarding the conception of the process and his opinion of its commercial possibilities.

Martin explained the initiation of the OXO process as follows: In the gasol fraction, they had large amounts of propene and butene for which they had no use, so Martin instructed his chemists to find some new use for these compounds, other than direct conversion to propyl and butyl alcohols. At first, experiments were made on adding these olefines to water gas, then passing the mixture through the normal Fischer-Tropsch catalyst chamber with the objective of producing high-octane motor fuel. This objective was not attained, since substantially, only aldehydes were produced. Results indicated that such a process might be most desirable for production of aldehydes with possible later reduction to alcohols, so from this start, the OXO process was developed.

Martin said that he considered the OXO process the best one available for production of aldehydes and alcohols with an upper limit of about C_{18}. From the hard paraffins of the Fischer-Tropsch process, alcohols and acids up to C_{25} could be produced by first chlorinating the wax, but aside from this production of very high molecular weight compounds, the OXO process was considered the best, both technically and economically, for manufacture of compounds, especially aldehydes and alcohols, to an upper limit of about C_{18}.

Production of Fatty Acids by Oxidation of Wax:

Martin then gave an account of their process for producing higher fatty acids by the oxidation of wax using nitrosyl sulphuric acid, of which full details were subsequently obtained from Dr. Velde (See Report 8). He claimed that among the advantages of this process over that used at Witten, was the successful treatment of hard wax to produce the higher acids and the absence from the product of hydroxy acids and esters. The process appealed to the Ruhrchemie, furthermore, because it represented a 'cross-link' with their synthetic nitrogen plant. They had carried out research on other 'cross-links' such as the nitration of the Fischer-Tropsch paraffins.

Reaction of Water Gas and Acetylene using Cobalt Catalyst:

Some tests were started on a pilot plant scale to find out what this reaction would produce. Possibly it was expected that acrylic aldehyde or its homologs might result. The total pressure was 20 atmospheres and, of this, acetylene accounted for about one atmosphere partial pressure. Water gas was present in about stoichimetrical quantity, while the remainder was inert gas. A cobalt catalyst had been used at a temperature of 100°C.. It was understood that this investigation was still in progress when the bombing stopped all research and that the results are far from complete. Definite evidence was obtained, however, that acetylene entered into the reaction.

Design of Fischer-Tropsch Catalyst Chambers:

Martin was asked why this had not made further progress in view of the fact that the present two standard designs (plate type and concentric-double-tube type) had been known before the war. He said that the construction companies making catalyst chambers (Gutehoffnungshutte, Mannesmann, Krupp, etc.) had decided to freeze the design in order to avoid changes in tools, patterns, etc. He said that Ruhrchemie itself had considered other designs, such as cooling liquids flowing over the catalyst, catalyst suspended in liquids, etc., but after consideration they always came back to present designs as preferable.

Martin said that Schaffgotsch Benzin had tried to do without the inner tube of the double-tube reactor and had experimented with the use of single tubes 20mm. i.d. The result, however, had been carbon deposition and excessive methane formation.

Recent Research:

Martin stated that practically no research work had been carried on by Ruhrchemie over the last 15 months because of the almost constant bombings. Not only was research personnel needed for other work in the plant, but they did not get sufficient sleep to carry on effective research work.

German Government Subsidy:

Martin said that only the primary products were protected by Government subsidy - not the various secondary products made.

Fischer-Tropsch Patents:

Martin said that the basic patents had expired, but many others had been in force that covered many details, modifications, and the working up of primary products.

Lurgi Patents Related to Fischer-Tropsch:

Martin said that the many Lurgi (Metallgesellschaft) patents related to Fischer-Tropsch process were mostly paper patents. The initiation of many of these patents resulted from the frequent visits of Lurgi engineers to the Fischer-Tropsch plants, where Lurgi had installed most of the active carbon units.

Personnel:

Martin stated that Dr. Roelen, Director of Research of Ruhrchemie, was at present ill and living on a farm near Salzwedle. His staff were in the vicinity of Salzgitte.